Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Photo-Induced Dynamic Processes in Perovskite Solar Cells: The Influence of Perovskite Composition in the Charge Extraction and the Carriers Recombination.

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S1. EXPERIMENTAL SECTION

FTO glass (Nippon Sheet Glass) was prepared by etching chemically and cleaned with detergent solution (Helmanex 5 vol% solution), acetone, and isopropanol. To form a 45 nm thick TiO_2 blocking layer, diluted titanium diisopropoxide bis(acetylacetonate) (TAA) solution (Sigma-Aldrich) in ethanol (0.4 ml of TAA in 9 ml of anhydrous isopropanol) was sprayed with oxygen gas at 450 °C. A 200-nm mesoporous TiO_2 was deposited on the substrate by spin coating at a speed of 2000 rpm for 10 s from a diluted TiO_2 paste (Dyesol-30NRD) in ethanol; the weight ratio of TiO_2 paste to ethanol is 1:9. After spin coating, the substrate was immediately dried on a hotplate at 100 °C, and the substrates were then heated at 500 °C for 20 min and cooled down. A DMSO solution of MAPbI and FAMAPbI precursors, 1.2M PbI_2 (TCI) and MAI (Dyesol) solution and 1.15 M PbI_2, 1.035 M MAI and 0.115 M FAI (Dyesol) solution were prepared, respectively. The $(FAPbI_3)0.85(MAPbBr_3)0.15$ precursor solution was prepared by mixing 1.1 M FAI, 1.15 M PbI2, 0.2 M MABr (Dyesol) and 0.2 M $PbBr_2$ (TCI) in a mixed solvent of DMF: DMSO = 4: 1 (volume ratio). For CsFAMAPbIBr solution, another solution of CsPbI3 was also prepared in DMSO. And then, these solutions were mixed as 5 vol% ratio. All of solutions were spin-coated at 1000 rpm for 10 s and continuously at 5000 rpm for 30 s in nitrogen glove box. After entering the second step, 100 µL of anhydrous trifluorotoluene was poured at 10 seconds before the finish. Perovskite films were annealed at 100 °C for 30 min. The hole transporting layer was prepared by a solution dissolving 91 mg of Spiro-OMeTAD (Merck) in 1 mL of chlorobenzene. As additives, 21 µL of Li-bis(trifluoromethanesulfonyl) imide solution (520 mg in 1 mL of acetonitrile), 16 µL of FK209 [tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III) tris(bis (trifluoromethylsulfonyl)imide) solution (400 mg in 1 mL of acetonitrile) and 36 µL of 4-tertbutylpyridine were added. The HTM solution was spin-coated at 4000 rpm for 20 s, and followed by the deposition of the 70 nm thick Au electrode by a thermal evaporation.

Solar cell characterization:

The current density vs voltage (J-V) curves were obtained using a Sun 200 solar simulator (150 W, ABET Technologies), with the appropriate filters to simulate the AM 1.5G solar spectrum. The light intensity was calibrated with a silicon photodiode (NREL) to obtain 100 $mW \cdot cm^{-2}$ of light intensity. The IV curves were registered with a Keithley digital 2400 Source Meter and plotted automatically with a home-built Labview© software. The scan rate conditions were 80.6 $mV \cdot s^{-1}$. PICE and TPV measurements were carried out using a white light LED ring LUXEON® Lumileds and the signal is measured in an oscilloscope Yokogawa DLM2052 registering drops in voltage. All measured Voc decays were performed in steady state according to the Voc stabilization time of each device.

S2. TOP VIEW AND CROSS-SECTIONAL SEM IMAGING.

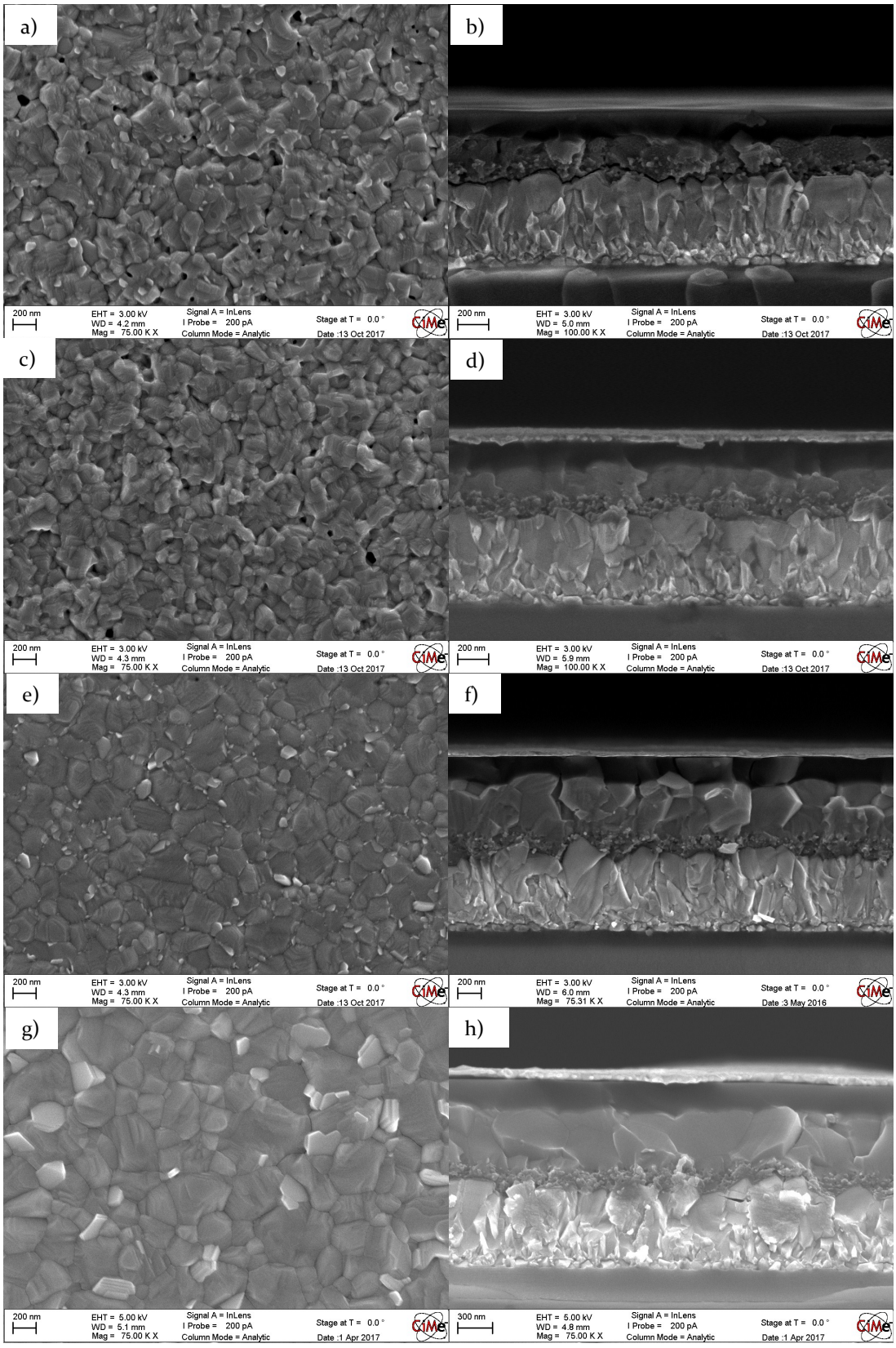

Figure S1. Top view and cross section SEM images for (a,b) MAPbI, (c,d) FAMAPbI, (e,f) FAMAPbIBr and (g,h) CsFAMAPbIBr structures.

S3. XRD CHARACTERIZATION.

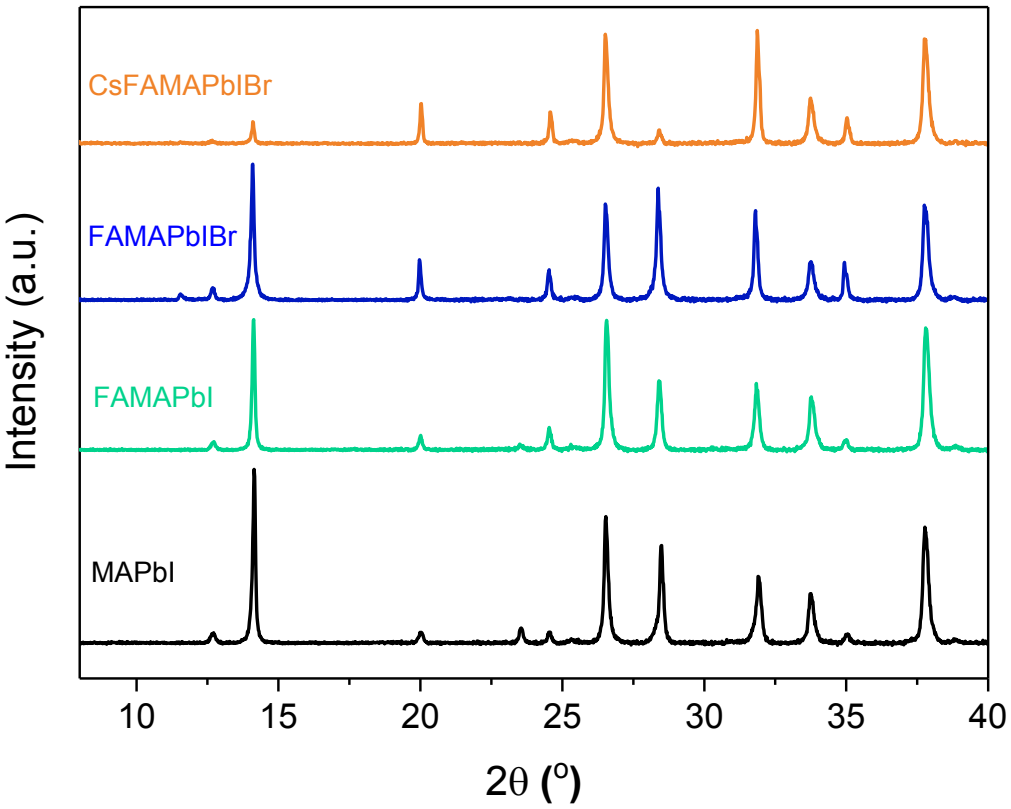

Figure S2. XRD patterns of the different perovskite composition.

S4. EFFICIENCY STATISTICS.

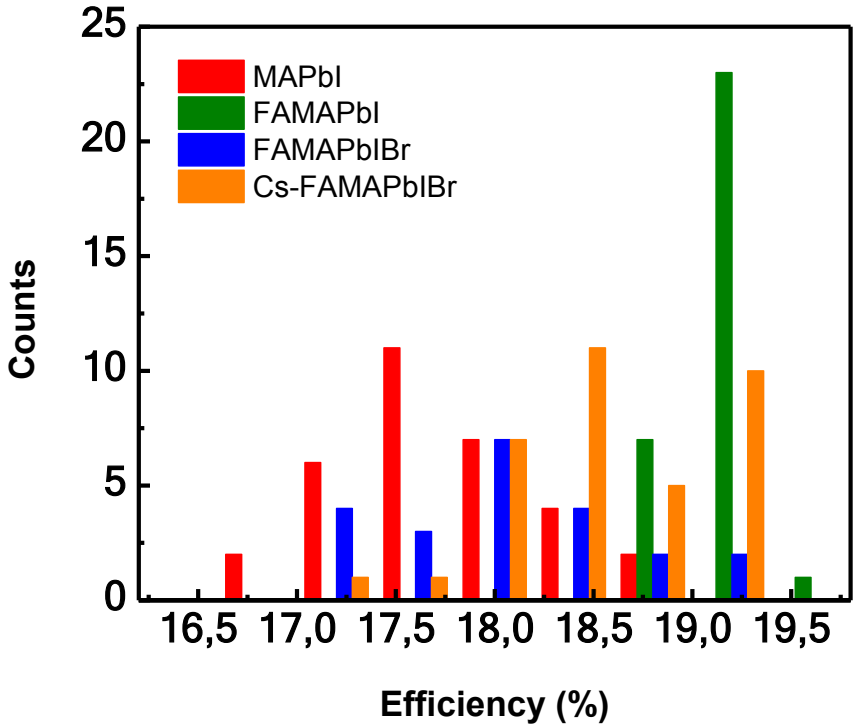

Figure S3. Efficiency statistics of respective MAPbI, FAMAPbI, FAMAPbIBr and Cs-FAMAPbIBr.

S5. PHOTO-INDUCED CHARGE EXTRACTION (PICE)

Description:

In photo induced charge extraction (PICE) the cell in open circuit conditions was illuminated at various light intensities using a white LED array. When a stable voltage was reached (see Figure S6), the LEDs were switched off and the cell was short circuited through a small resistance (50 Ω) simultaneously. In parallel to this resistance an oscilloscope (Yokogawa DLM2052) measured a voltage profile, which integrated and divided by the known resistance (50 Ω) gives the extracted charge. In order to exclude charge extraction losses by recombination we can verify that the extraction kinetic is faster than the recombination one at 1 sun illumination.

PICE decays at different light intensities:

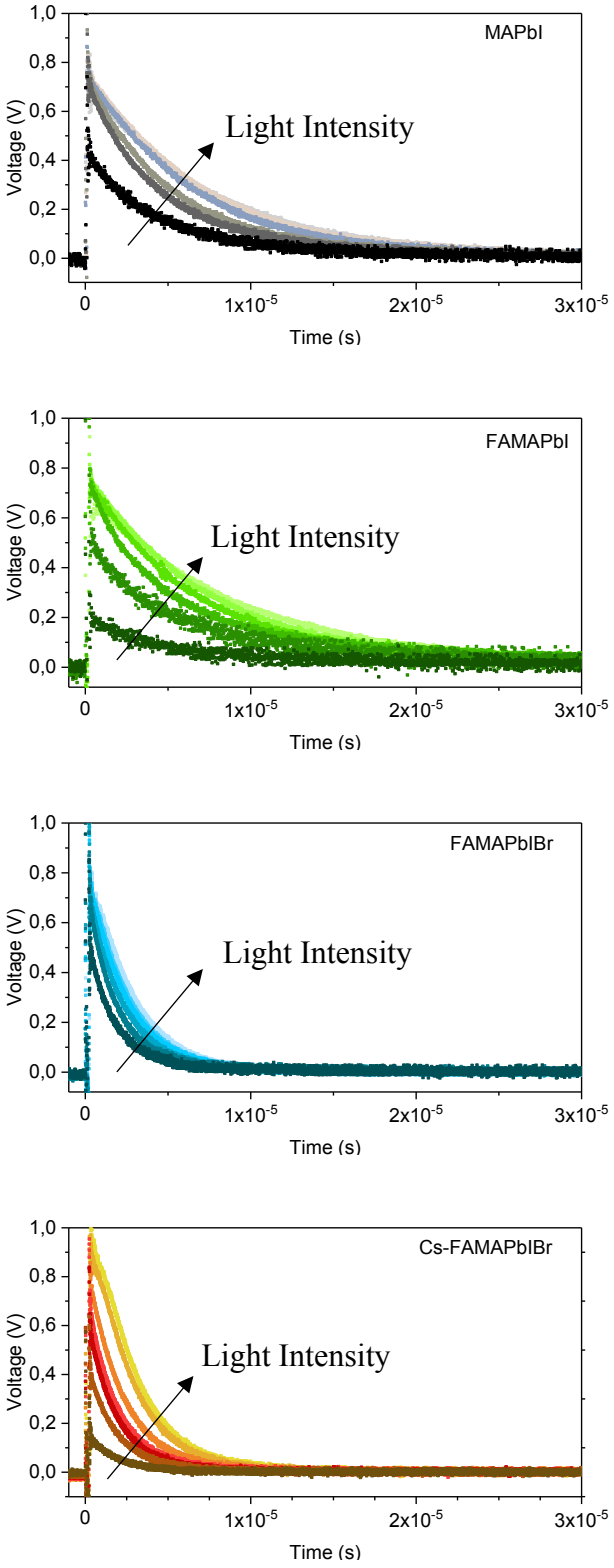

Figure S3. Photo-Induced Charge Extraction Voltage decays at different light intensities.

S1. PHOTO-INDUCED TRANSIENT PHOTO-VOLTAGE (PI-TPV)

Description:

In photo induced transient photovoltage (PI-TPV) the cell was illuminated with a white LED array until stable open circuit voltage, then, keeping the cell in open circuit, a small perturbation was added using a monochromatic light (600 nm) pulse using a nanosecond PTI GL-3300 nitrogen laser. The consequent open circuit voltage transient was registered with a Yokogawa DLM2052 oscilloscope. This measurement was performed at various LED array luminance. Voltage transients were fitted with an exponential function.